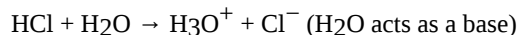
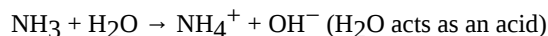


12.6: Autoionization of Water

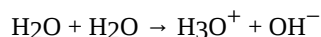
Learning Objectives

- Describe the autoionization of water.
- Calculate the concentrations of H^+ and OH^- in solutions, knowing the other concentration.

We have already seen that H_2O can act as an acid or a base:



It may not be surprising to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:



This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ in a sample of pure H_2O is about 1.0×10^{-7} M. If we use square brackets—[]—around a dissolved species to imply the molar concentration of that species, we have

$$[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14} :

$$[\text{H}^+] \times [\text{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

In acids, the concentration of $\text{H}^+(\text{aq})$ — $[\text{H}^+]$ —is greater than 1.0×10^{-7} M, while for bases the concentration of $\text{OH}^-(\text{aq})$ — $[\text{OH}^-]$ —is greater than 1.0×10^{-7} M. However, the *product* of the two concentrations— $[\text{H}^+][\text{OH}^-]$ —is *always* equal to 1.0×10^{-14} , no matter whether the aqueous solution is an acid, a base, or neutral:

$$[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_{w} :

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

This means that if you know $[\text{H}^+]$ for a solution, you can calculate what $[\text{OH}^-]$ has to be for the product to equal 1.0×10^{-14} , or if you know $[\text{OH}^-]$, you can calculate $[\text{H}^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_{w} .

✓ Example 12.6.1

What is $[\text{OH}^-]$ of an aqueous solution if $[\text{H}^+]$ is 1.0×10^{-4} M?

Solution

Using the expression and known value for K_{w} ,

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[\text{OH}^-]$$

We solve by dividing both sides of the equation by 1.0×10^{-4} :

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} \text{ M}$$

It is assumed that the concentration unit is molarity, so $[\text{OH}^-]$ is 1.0×10^{-10} M.

? Exercise 12.6.1

What is $[H^+]$ of an aqueous solution if $[OH^-]$ is $1.0 \times 10^{-9} \text{ M}$?

Answer

$$1.0 \times 10^{-5} \text{ M}$$

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of H^+ or OH^- ions in the formula unit because $[H^+]$ or $[OH^-]$ may not be the same as the concentration of the acid or base itself.

✓ Example 12.6.2

What is $[H^+]$ in a 0.0044 M solution of $Ca(OH)_2$?

Solution

We begin by determining $[OH^-]$. The concentration of the solute is 0.0044 M, but because $Ca(OH)_2$ is a strong base, there are two OH^- ions in solution for every formula unit dissolved, so the actual $[OH^-]$ is two times this, or $2 \times 0.0044 \text{ M} = 0.0088 \text{ M}$. Now we can use the K_w expression:

$$[H^+][OH^-] = 1.0 \times 10^{-14} = [H^+](0.0088 \text{ M})$$

Divide both sides by 0.0088:

$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12} \text{ M}$$

$[H^+]$ has decreased significantly in this basic solution.

? Exercise 12.6.2

What is $[OH^-]$ in a 0.00032 M solution of H_2SO_4 ? (Hint: assume both H^+ ions ionize.)

Answer

$$1.6 \times 10^{-11} \text{ M}$$

For strong acids and bases, $[H^+]$ and $[OH^-]$ can be determined directly from the concentration of the acid or base itself because these ions are 100% ionized by definition. However, for weak acids and bases, this is not so. The degree, or percentage, of ionization would need to be known before we can determine $[H^+]$ and $[OH^-]$.

✓ Example 12.6.3

A 0.0788 M solution of $HC_2H_3O_2$ is 3.0% ionized into H^+ ions and $C_2H_3O_2^-$ ions. What are $[H^+]$ and $[OH^-]$ for this solution?

Solution

Because the acid is only 3.0% ionized, we can determine $[H^+]$ from the concentration of the acid. Recall that 3.0% is 0.030 in decimal form:

$$[H^+] = 0.030 \times 0.0788 = 0.00236 \text{ M}$$

With this $[H^+]$, then $[OH^-]$ can be calculated as follows:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.00236} = 4.2 \times 10^{-12} \text{ M}$$

This is about 30 times higher than would be expected for a strong acid of the same concentration.

? Exercise 12.6.3

A 0.0222 M solution of pyridine ($\text{C}_5\text{H}_5\text{N}$) is 0.44% ionized into pyridinium ions ($\text{C}_5\text{H}_5\text{NH}^+$) and OH^- ions. What are $[\text{OH}^-]$ and $[\text{H}^+]$ for this solution?

Answer

$$[\text{OH}^-] = 9.77 \times 10^{-5} \text{ M}; [\text{H}^+] = 1.02 \times 10^{-10} \text{ M}$$

Summary

In any aqueous solution, the product of $[\text{H}^+]$ and $[\text{OH}^-]$ equals 1.0×10^{-14} (at room temperature).

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